Stabilizing Lithium-Metal Anode by Interfacial Layer

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June 13, 2019

Project ID
#bat365

Overview

Timeline

- Start: Oct. 1, 2017
- End: Sep. 30, 2020
- Percent complete: 50%

Budget

- Total project funding
  $1,200,000
- Funding received in FY 2018
  $300,000
- Funding for FY 2019
  $450,000

Barriers

- Barriers addressed
- Cost (A)
  Addressing the cost barrier requires developing lower-cost processing methods.
- Performance (C)
  Much higher energy densities are needed to meet both volume and weight targets.
- Life (E)
  Battery must provide significant energy over the life of the vehicle .

Partners

- Collaboration
- Professor Jian Qin (Stanford)
- Professor Steve Chu (Stanford)
- Dr. Michael Toney (SLAC)

Project Objective and Relevance

Objectives

- Develop lithium metal anodes with high capacity and reliability for next-generation rechargeable batteries to power electric vehicles.
- Explore the rational design of novel interfacial layers between lithium metal and electrolytes to overcome the intrinsic material challenges that lead to short battery life, including lithium metal dendrite formation and severe side chemical reactions during electrochemical cycling.
- Understand the effects of interfacial protection materials on the performance and life time of lithium metal batteries.
- Develop scalable low-cost methods for the synthesis of interfacial protection materials.

-Project contents are directly aimed at the listed barriers: high cost, low energy density and short battery life.

Approach/Strategy

Advanced design and synthesis of interfacial protecting layers

1)Engineer various interfacial protection materials with excellent chemical and mechanical stability, both inorganic and polymeric, to suppress lithium dendrite formation during electrochemical cycling and to improve Coulombic efficiency.

2)Develop/discover stable, light-weight host materials with high lithium affinity for the fabrication of nanoporous lithium-host composite electrodes with minimum relative volume change during cycling and improved electrochemical performance.

Structure and property characterization

1) Ex-situ transmission electron microscopy & scanning electron microscopy
2) In-situ transmission electron microscopy
3) Cryo electron microscopy
4) In-situ optical microscopy
5) X-ray diffraction
6) X-ray photoelectron spectroscopy
7) Fourier transform infrared spectroscopy

Electrochemical testing

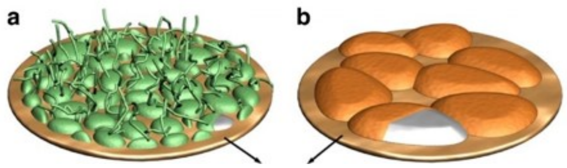
1) Coin cells and pouch cells
2) A set of electrochemical techniques (ultramicroelectrode, etc.)

Milestones for FY19

Month/ year	Milestones	Status
12/2018	Understand of factors controlling Li deposition systematically (solvation effect)	Complete
3/2019	Extend learning to modified polymer coating design	Complete
6/2019	Characterize modified polymer coating	On track
9/2019	Testing coatings on Li metal in Li/NMC full cells	On track

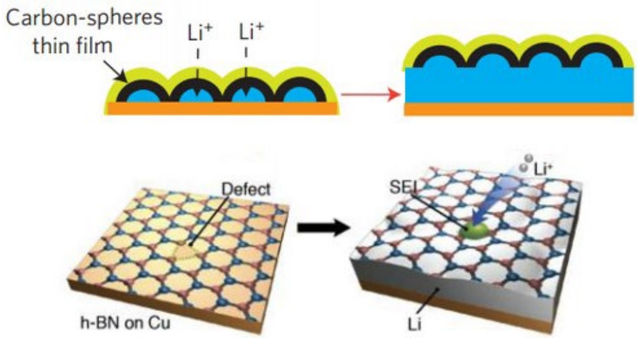
Previous Approaches/Strategies for Lithium Metal Anodes

Electrolyte Tuning



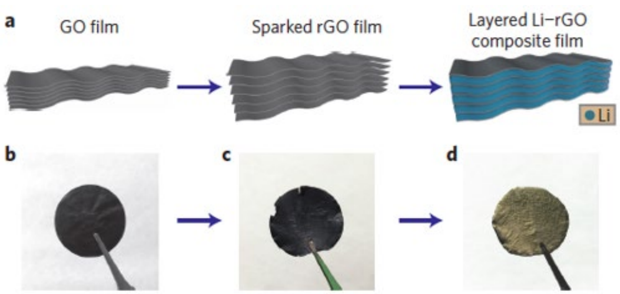
Nature Commun. **6**, 7436 (2015)
Proc. Natl. Acad. Sci., **114,** 12138 (2017)

Artificial SEI Engineering



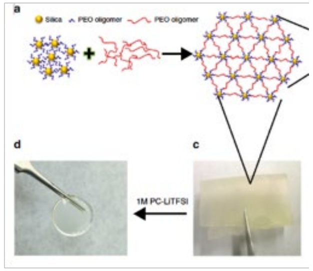
Nat. Nanotechnol. **9**, 618 (2014)
Nano Lett. **14**, 6016 (2014)
Nat. Energy **1**, 16010 (2016)

Li Hosts & Scaffolding



Nat. Commun. **7**, 10992 (2016)
Nat. Nanotechnol. **11**, 626 (2016)
Sci. Adv. **3,** e1701301 (2017)

Tough Polymer/Gel Electrolyte



Kotov, N. A., *et al. Nature Commun.* **2015**, *6*, 6152
Archer, L. A., *et al. Nat. Commun.* **2015**, *6*
Lin, D., *et al. Adv. Mat.* **2016.**

Tough vs. Soft Polymers for Li metal

Tough, high modulus polymers suffer from poor contact with Li metal during deposition and stripping.

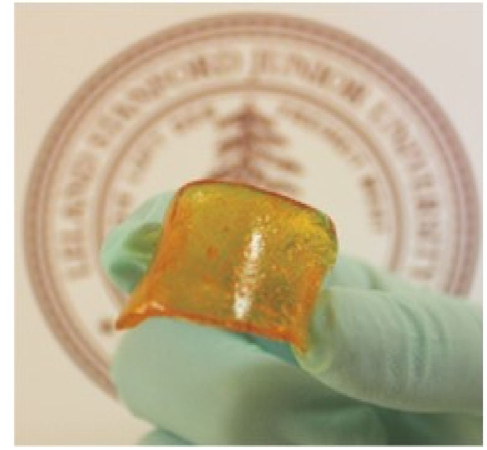
Soft, flowable viscoelastic polymers can accommodate volume change and preserve the polymer-Li interface.

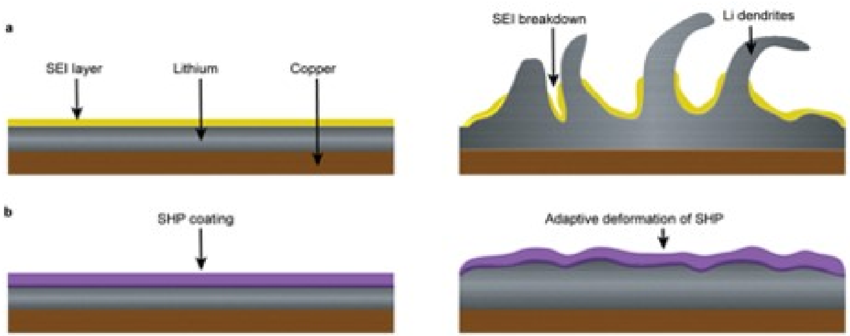
Previous Accomplishment

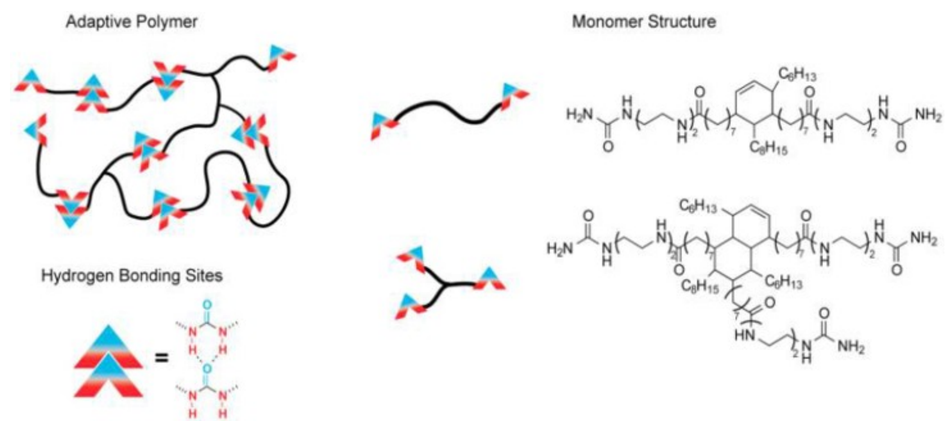
Soft, dynamic polymer coating for Lithium – Self-healing polymer

Self-healing polymer (SHP)

- Viscoelastic supramolecular polymer
- Low glass transition temperature
- Promotes uniform Li deposition





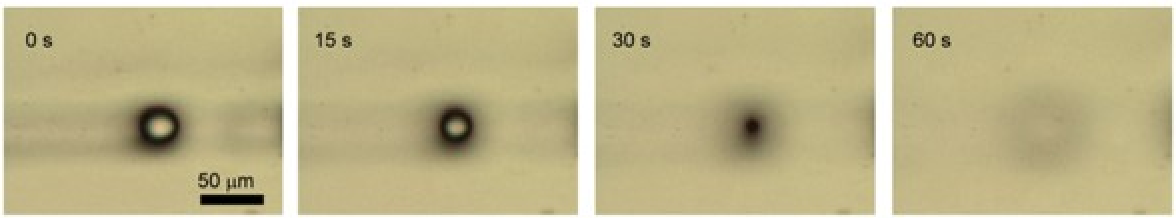


ACS Energy Lett. 1247–1255 (2016)

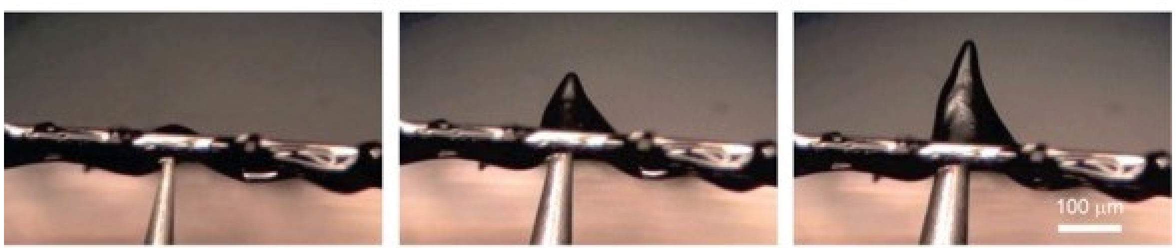
Previous Accomplishment

Soft, dynamic polymer coating for Lithium – Self-healing polymer

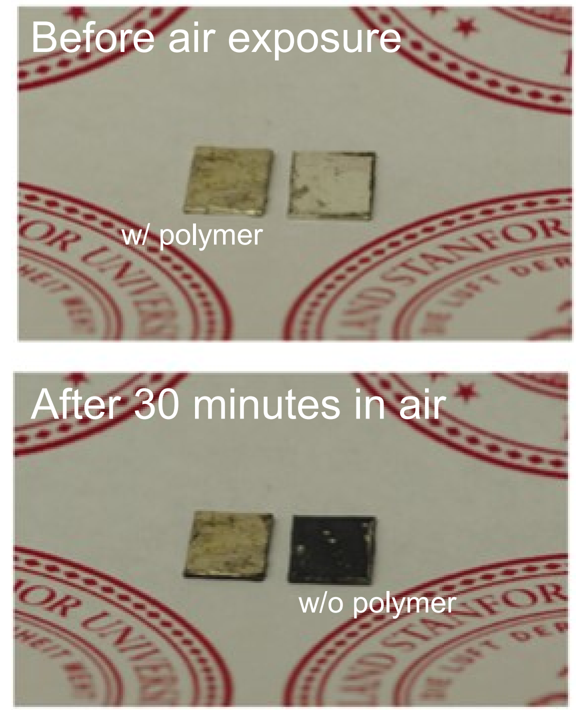
Rapid healing of pinhole in polymer film
(Ensures uniform coating of Li)



Conformal coating of high aspect ratio structure
(Dendrite or filamentary Li analogue)



Air stable coating of Li metal

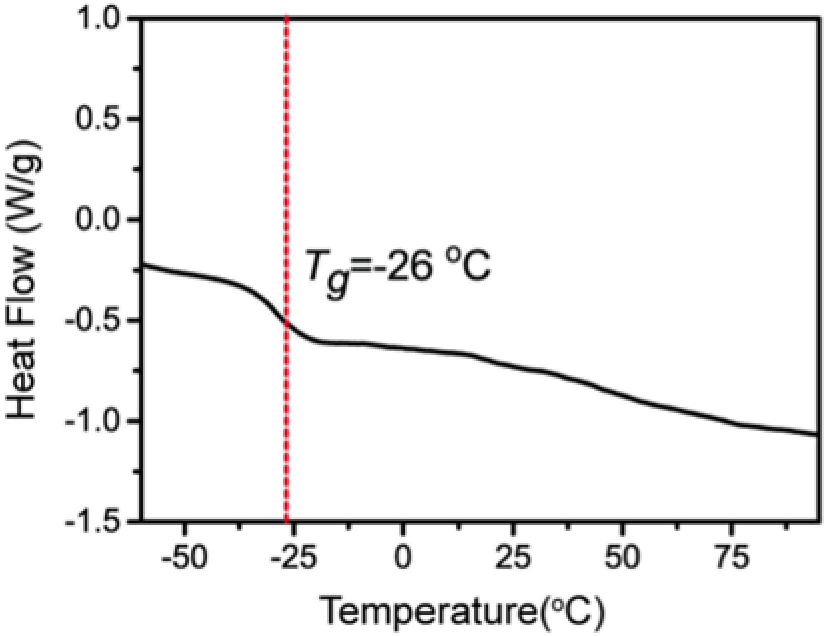


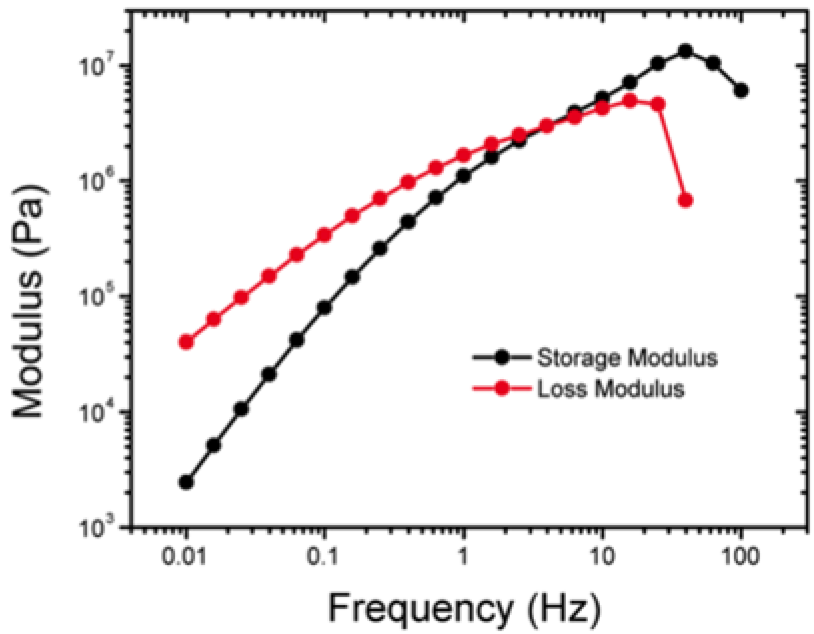
ACS Energy Lett. 1247–1255 (2016)

Previous Accomplishment

Soft, dynamic polymer coating for Lithium – Self-healing polymer

Soft, viscoelastic coating is flowable at room temperature.
It can conformally coat uneven Li growths and cracks in SEI.



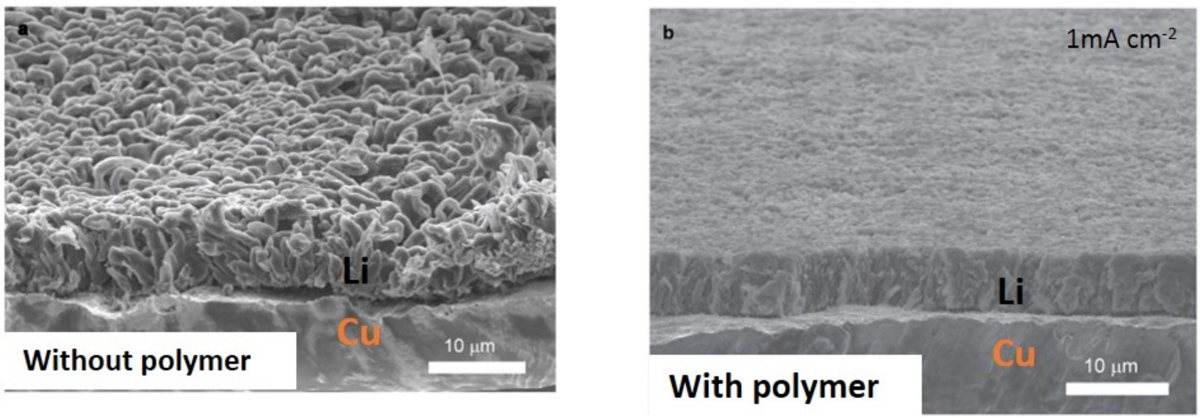


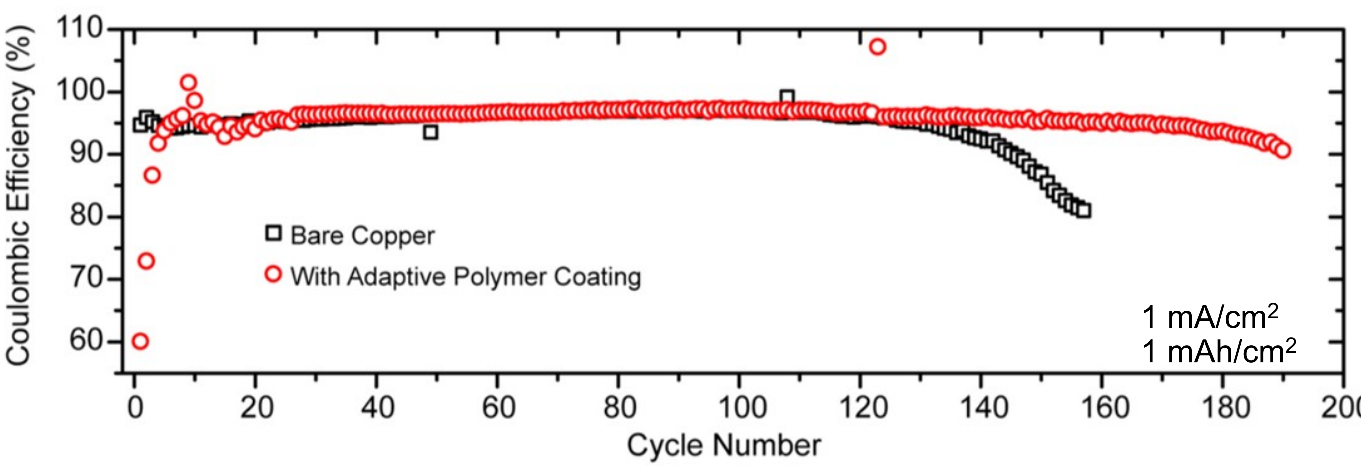
ACS Energy Lett. 1247–1255 (2016)

Previous Accomplishment

Soft, dynamic polymer coating for Lithium – Self-healing polymer

- Li deposited on Cu without the polymer coating is high-aspect ratio, promoting side reactions through high surface area.
- Li deposited with the polymer coating is **dense, compact, and uniform.**





1M LiTFSI
1 wt% $LiNO_3$
DOL/DME
75 uL

Li|Cu, strip to 1 V

ACS Energy Lett. 1247–1255 (2016)

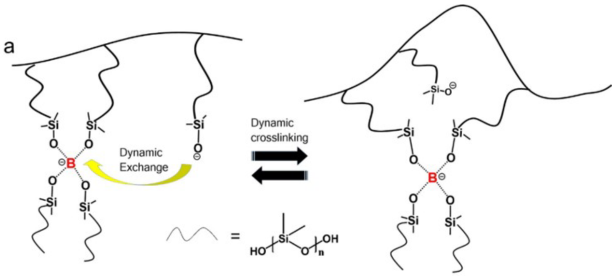
Previous Accomplishment

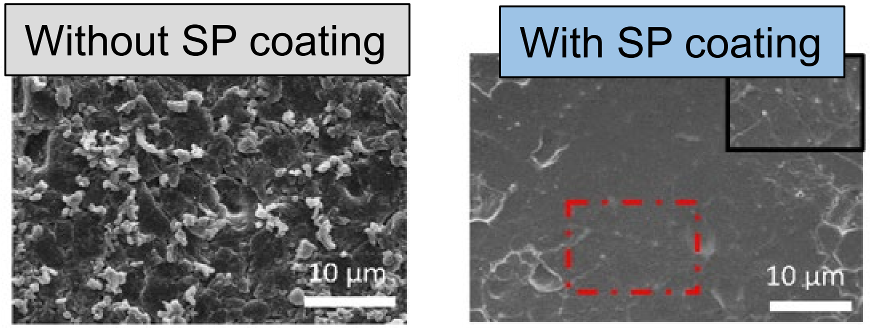
Soft, dynamic polymer coating for Lithium – "Solid-liquid" hybrid

Silly Putty (SP)

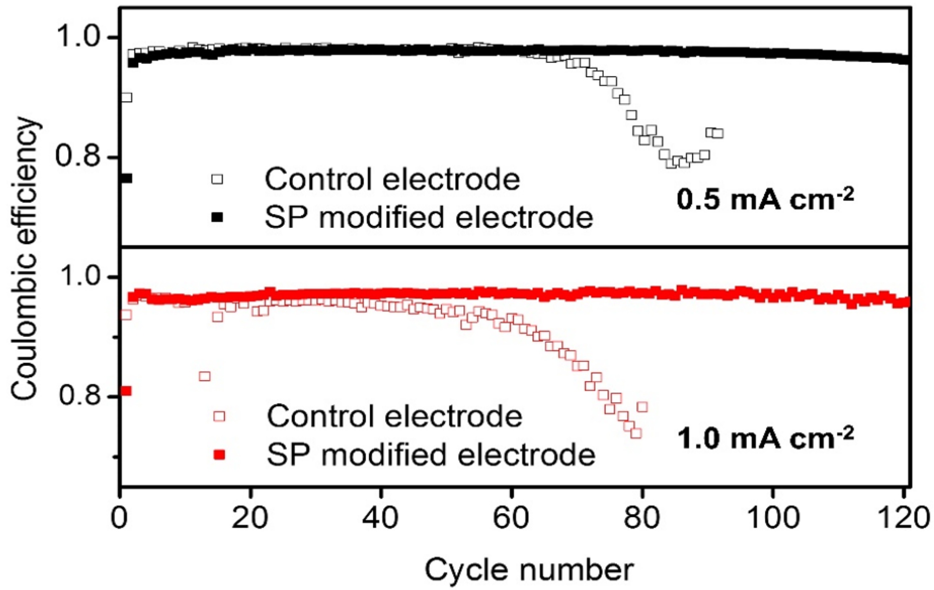
- Liquid-like at rest
- Solid-like upon stress

Dynamic crosslinks enable flowability while providing mechanical stiffness upon dendrite growth.





After 75 cycles



1M LiTFSI
1 wt% $LiNO_3$
DOL/DME
60 uL

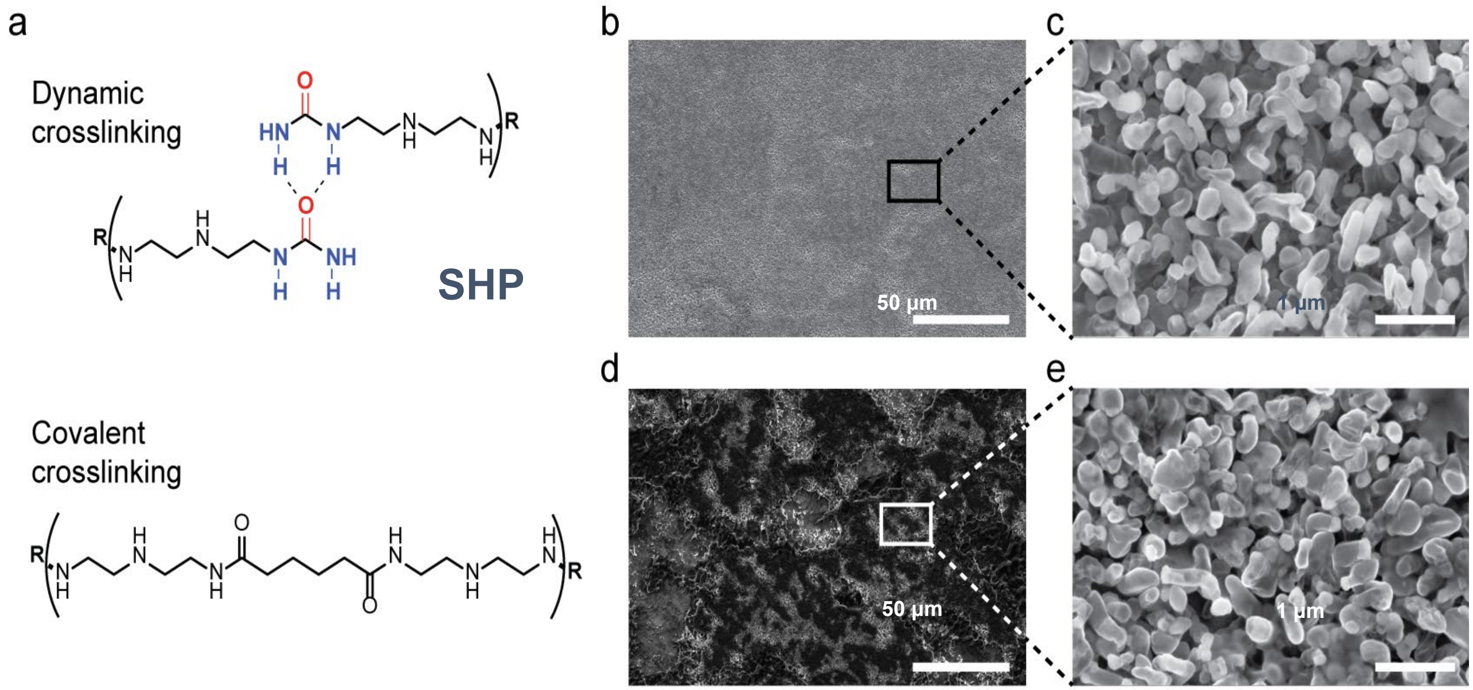
Li|Cu, strip to 2 V

J. Am. Chem. Soc. 139, 4815 (2017)

Accomplishment and Progress

Developed understanding of roles of polymer mechanics and polymer chemistry on Li metal deposition

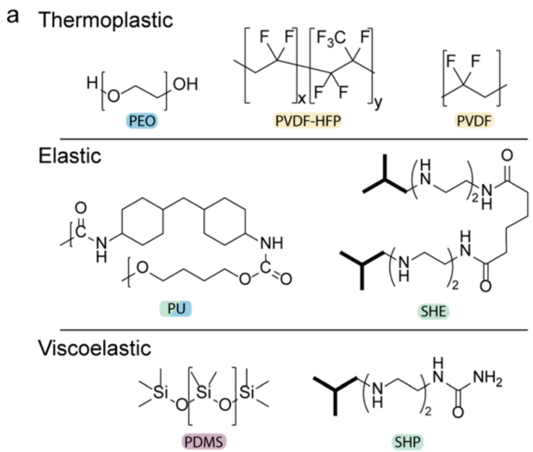
- Polymer mechanics / film quality influences deposition uniformity on the electrode scale.



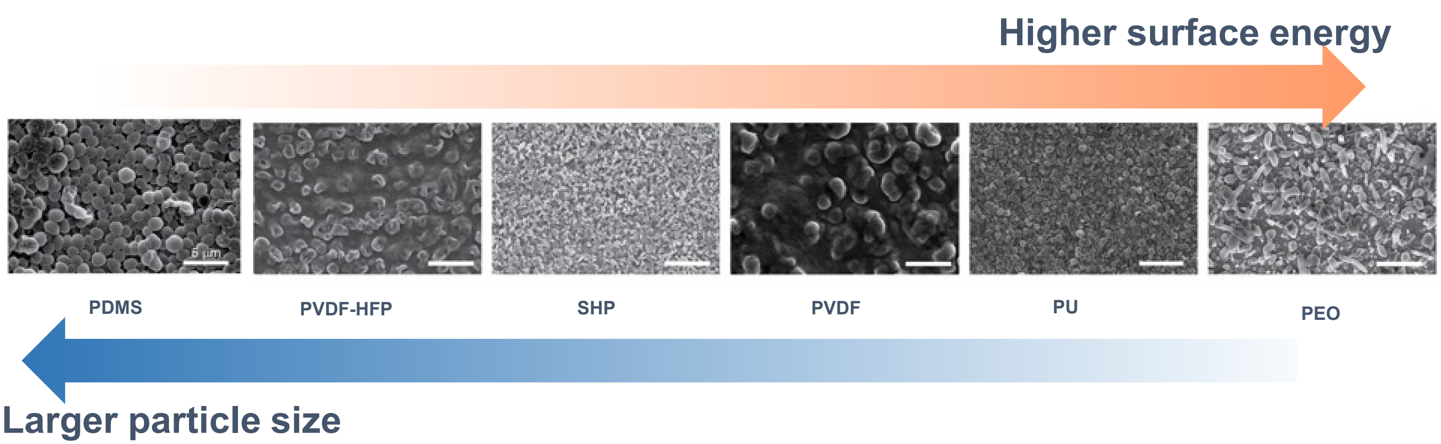
J. Am. Chem. Soc. 2018, 140, 11735−11744

Accomplishment and Progress

Developed understanding of roles of polymer mechanics and polymer chemistry on Li metal deposition



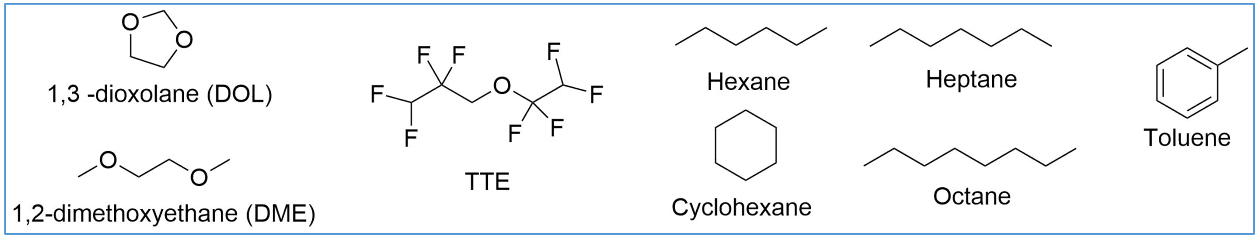
- Polymer chemistry determines Li morphology microscopically
- A polymer with less interaction with the Li surface would stabilize the interface less
- Lesser interaction/reactivity promote the growth of larger particles (less interface)



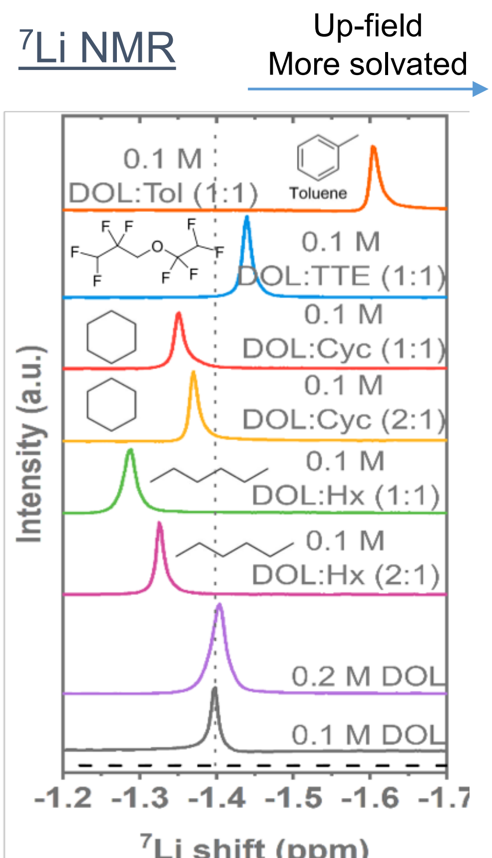
J. Am. Chem. Soc. 2018, 140, 11735−11744

Accomplishment and Progress

Use model systems to study solvation effect on Li metal deposition

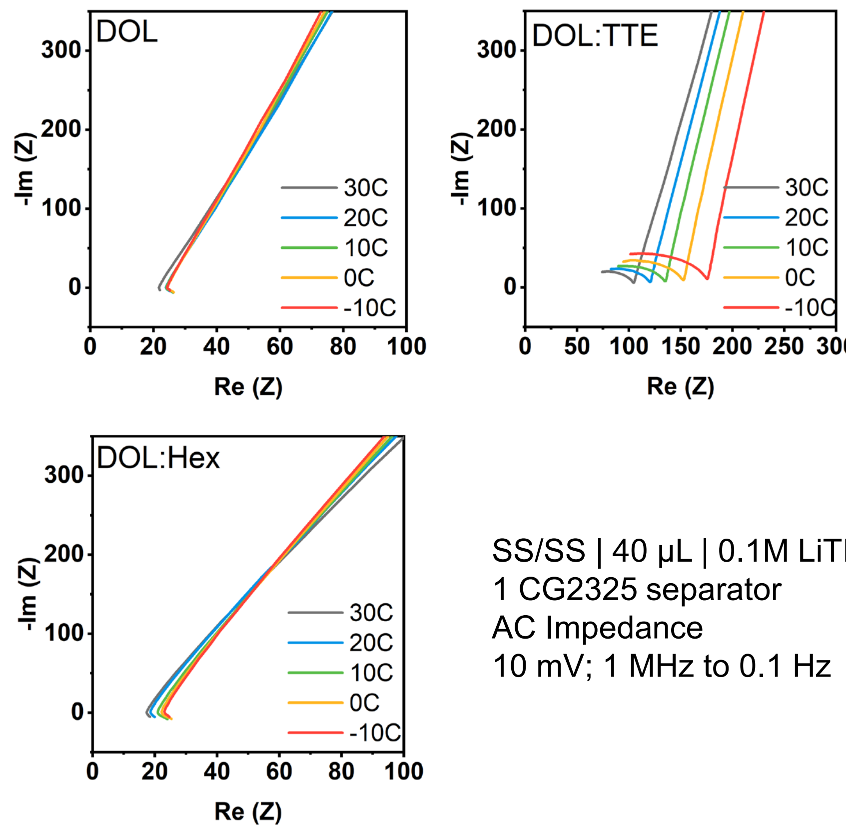


^{7}Li NMR



0.1M LiTFSI
Capillary NMR setup
100 μL sample in capillary
1M $LiClO_4$ in CD_3CN deuterated solv.

Impedance

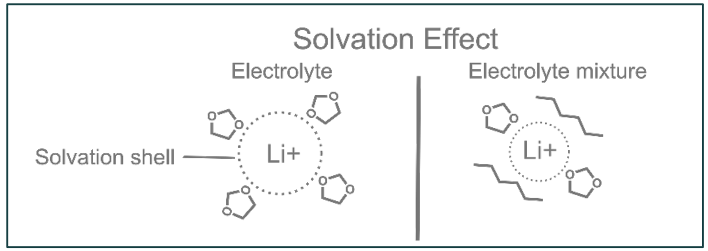


SS/SS | 40 μL | 0.1M LiTFSI
1 CG2325 separator
AC Impedance
10 mV; 1 MHz to 0.1 Hz

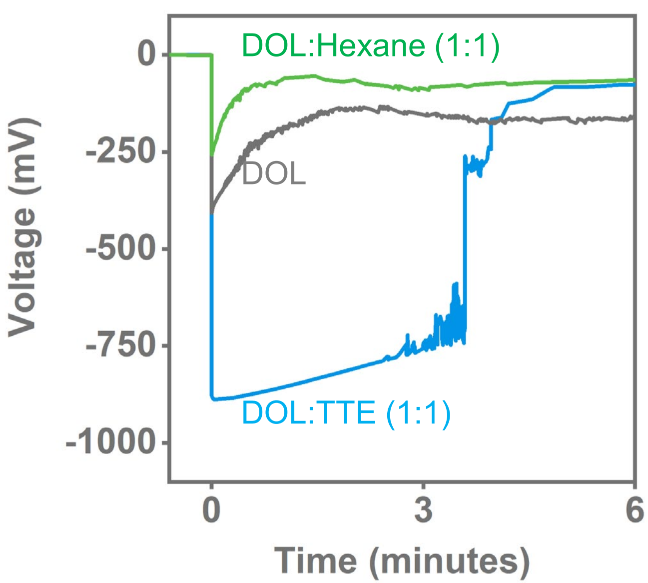
Submitted (2019)

Accomplishment and Progress

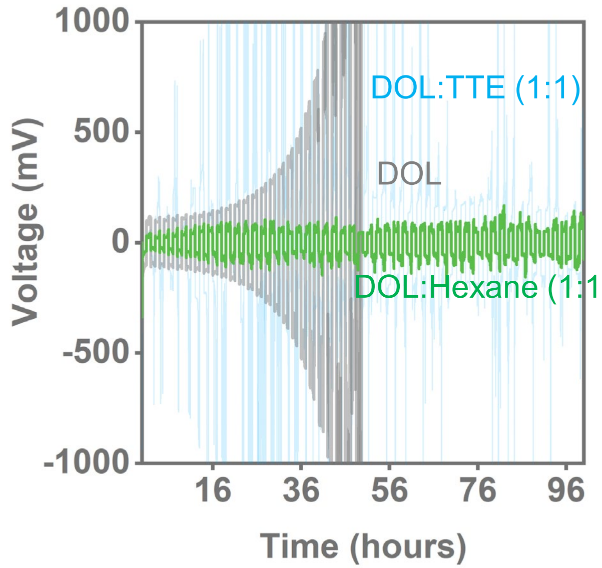
Less solvated Li+ lower overpotential for Li deposition, more plate-like Li growth



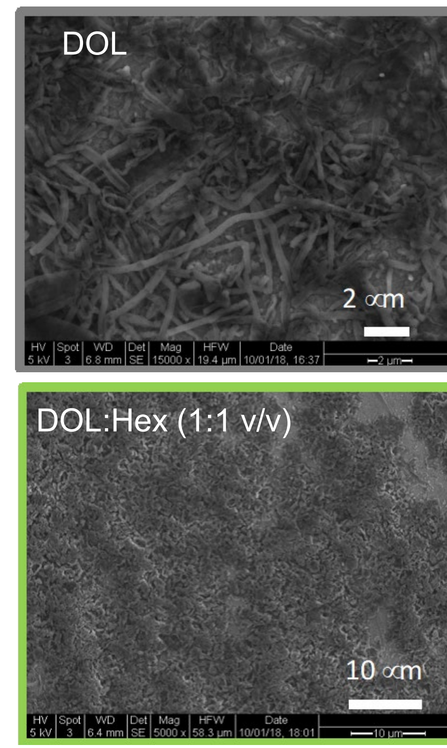
- Lower nucleation and growth overpotentials



Prolonged cycling



Li morphology changed

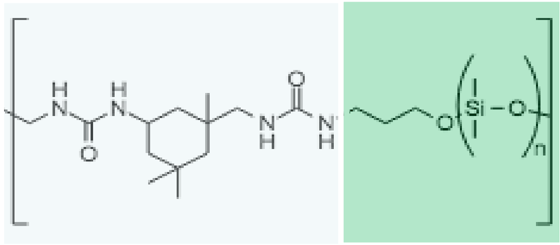


Li/Li
Current rate: 1 mA/cm^2
Capacity: 1 mAh/cm^2

Submitted (2019)

Accomplishment and Progress

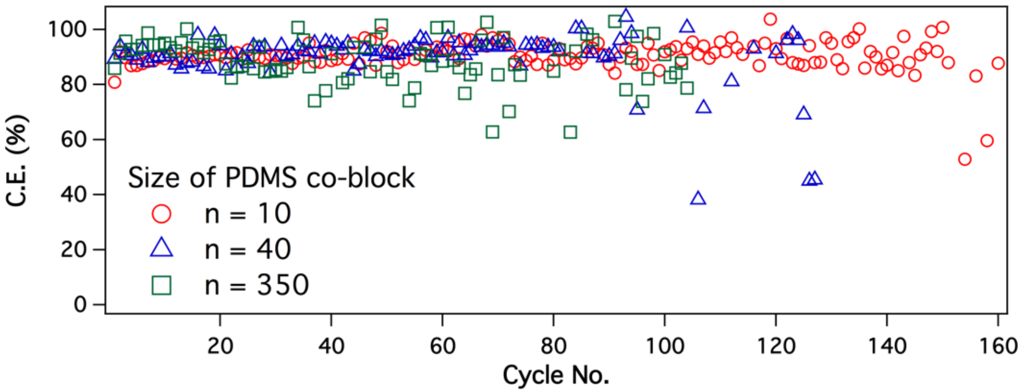
Polymer design that combines: low reactivity, low Li+ solvation, and flowable property



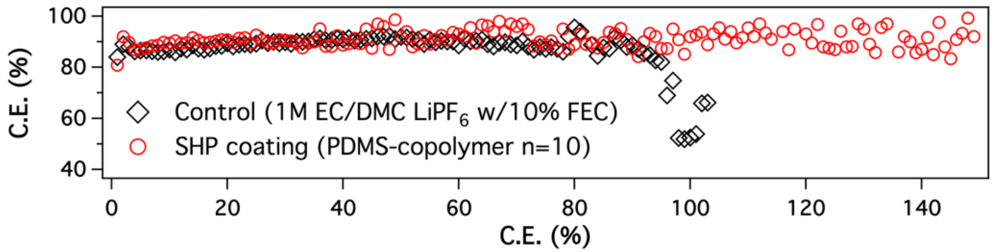
Hard Segment

Soft Segment

Coulombic Efficiency



<u>Ongoing work:</u>
Systematically vary the dynamics of the polymer



Responses to Previous Year Reviewers' Comments

Not applicable

Collaboration and Coordination

Dr. Mike Toney

Prof. Jian Qin
Dr. Steven Chu

Remaining Challenges and Barriers

- Coulombic efficiency is still not high enough to minimize lithium loss during extended cycles.

- It remains challenging to maintain even Li deposition and good cycling stability of lithium metal under high current density.

- Further studies are necessary to maintain a stable SEI when cycling lithium metal at high areal capacity.

- Coating polymers directly on Li metal can be challenging; solvent-free or direct methods may be required.

Proposed Future Work

FY 2019

- To elucidated interplay between critical parameters (chemical reactivity, solvation and polymer dynamics, etc.) for designing polymers which enable functional Li metal coatings.
- Design improved polymer systems based on learnings
- Testing promising polymer coatings in lean electrolyte, thin Li foil

FY 2020

- To understand the effect of interfacial SEI components and structure on Li/Li^+ kinetics and cycling performance (*e.g.* using cryo-EM).
- Investigate the effect of using flowable single-ion conductor
- To further improve the Coulombic efficiency of lithium metal cycling in both ether and carbonate based electrolyte

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity lithium anodes from the perspective of polymer design to enable the next-generation lithium metal-based batteries to power electric vehicles, which is highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced polymer design synthesis, characterization, battery assembly and testing, which has been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include demonstrating a completely new approach for interface layer for protection of lithium metal anodes, systematic understanding, using rational materials design, synthesizing and testing, and developing scalable and low-cost methods. The results have been published in top peer-reviewed scientific journals.
- **Collaborations and Coordination:** The PIs have established a number of highly effective collaborations.
- **Proposed Future Work:** Rational and exciting future has been planned.